

# SCIENCE FOR CERAMIC PRODUCTION

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## MECHANISM FOR COMPENSATING SLIP VOLUME CHANGES DURING HOT CASTING OF CERAMIC

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It is shown that during hot casting of ceramic the slip volume changes in the thermoplastic state, which comprise up to 85% of the total shrinkage, can be compensated by plastic deformation of the casting. The pressure gradient produced in the casting as it solidifies will determine the completeness of the compensation of the volume changes in the slip.

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Casting of thermoplastic slips is still the main method of producing articles with a complicated shape as well as tubular and rod-shaped articles. This technology is characterized by relative simplicity of implementation and high capacity, which is very important for organizing mass production. The technological formation cycle in this method, which includes filling the shaping cavity and holding under pressure, allows highly concentrated dispersed systems in which temporary thermoplastic process binders are used as the dispersed phase [1, 2].

A characteristic feature of a casting system of this type is that the density of the slip changes during cooling. This is expressed as a decrease of the slip volume — the slip shrinks. In general, when the casting system is heated to a temperature above the melting point and cooled to a temperature below the solidification (crystallization) point, the volume changes in the slip can be regarded as occurring in three stages: in the liquid state during cooling from the heating to the crystallization temperature; with a change in the aggregate state from a liquid into a solid; in the solid state with cooling from the crystallization temperature to the cooling temperature (ordinarily the room temperature). These stages are all characterized by definite external manifestations. They depend on a number of factors and are closely interrelated.

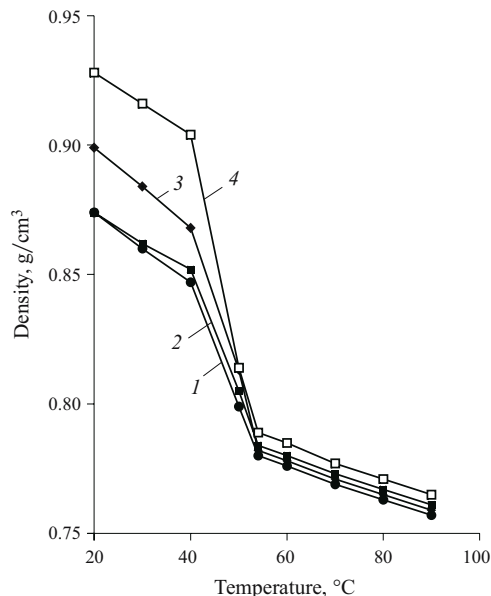
At the first stage the magnitude of the volume changes depends mainly on the thermal expansion coefficient of the slip in the liquid state and the overheating temperature. These volume changes are manifested externally (depending

on the cooling conditions) either in subsidence of the top surface of the slip or in the formation of internal voids. At the second stage the volume changes are determined, as a rule, by the nature, composition, and properties of the thermoplastic binder. The external manifestation consists in the formation of subsidence pits and loose material. At the third stage the magnitude of the volume changes depends on the thermal expansion coefficient of the slip in the solid state and the final casting temperature. The shrinkage at this stage decreases the external dimensions of the casting as compared with the corresponding dimensions of the mold. Thus, the shrinkage during hot casting is mainly determined by the characteristics of the dispersed system, more precisely, by the dispersed phase — the thermoplastic binder.

During hot casting the process temperature range of the slip falls within quite wide limits (20–80°C). Since the thermoplastic components of the binder in this temperature interval change the aggregate state and the thermal volume expansion coefficient of liquid media is tenths of a percent per degree, the volume change of the dispersed medium during casting can be very substantial. Undoubtedly, this should affect the volume–phase ratios in the slip and, correspondingly, the casting quality. In this connection, the temperature dependences of the density of the binders and their components in the temperature interval 20–95°C were determined to evaluate the real magnitudes of the volume changes in casting systems.

The density of the thermoplastic binders in the melted state was measured on a special setup consisting of two U-shaped manometers placed in thermostats. A liquid (wa-

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**Fig. 1.** Variation of the density of binders and their components versus temperature: 1) 99% paraffin + 1% oleic acid; 2) 96% paraffin + 4% wax; 3) 100% paraffin; 4) 91% paraffin + 6% wax + 3% oleic acid.

ter) with known density  $\rho_1$  is poured into one manometer and the experimental substance with density  $\rho_2$  is poured into the other one. After thermostating at a prescribed temperature for 2–3 h, an excess pressure is produced in the system. This gives rise to a difference in the levels  $h_1$  and  $h_2$  in the manometers.

The density of the experimental melt at the prescribed temperature was calculated from the relation

$$\rho_2 = \rho_1 \frac{h_1}{h_2}. \quad (1)$$

The density was determined to within 0.5%. Curves of the density versus the temperature are presented in Fig. 1 for certain compositions used in practice.

A comparative analysis of the cooling curve of paraffin (the main component of the binder) and the cooling curves of other binder compositions shows that they are in quite good agreement. In all cases three linear sections stand out. These sections correspond to the volume thermal expansion coefficient ( $K^{-1}$ ):  $(1.2 - 1.3) \times 10^{-3}$  — the interval below 40°C;  $(5.7 - 7.5) \times 10^{-3}$  — the interval of crystallization; and,  $(0.45 - 0.68) \times 10^{-3}$  — the interval above 55°C. The increment to the density coefficient of the binder is 1.20 during cooling, 1.02 during cooling to 55°C (conventionally chosen as the crystallization onset temperature), 1.14 during crystallization (55–40°C), and 1.03 during cooling from 40 to 20°C. Thus, the increment to the density coefficient in the thermoplastic state (below 55°C) is 1.17.

For casting systems based on, for example, BeO and a thermoplastic binder, these increment coefficients are

1.05–1.06 (the increment is about 1.01 in the liquid state and 1.05 in the solid-plastic state). A small additional decrease of this ratio (about fractions of a percent) can be achieved by varying the composition of the binder.

The main manifestations of the volume changes of the slip during cooling are external shrinkage  $W_{ex}$  (change in the dimensions of the casting as compared with the dimensions of the mold) and internal shrinkage  $W_{in}$  (total volume of the internal pits, loose material, and finely dispersed porosity; this volume is expressed as a percentage of the casting volume). However, the total external and internal shrinkage of the casting is not the magnitude of the total shrinkage, since a part of the slip volume changes occurring as the slip cools in the mold is compensated by the inflow of slip from the outside (under pressure) and a change in the volume of the mold, which increased as a result of the mold being heated during the casting process. Therefore, to obtain a complete estimate of the volume changes occurring during the formation of the casting, it is also necessary to take account of the compensated part  $W_c$  of the shrinkage. For this, the ratio of the internal to the compensated shrinkage was used as a quantitative criterion which makes it possible to evaluate objectively the rationality of the casting technology developed:

$$\psi = \frac{W_{in}}{W_c},$$

where  $\psi$  is a dimensionless coefficient characterizing the rationality of the technology.

The greater the value of  $\psi$ , the higher the uncompensated shrinkage, leading to a changing the dimensions of the casting, formation of pits and loose material, internal stresses and cracks, i.e., to lower casting quality, is. Therefore, large values of  $\psi$  show that the casting parameters are incorrect. Thus, in order to choose effective process regimes for solidification of the casting it is necessary to have a clear understanding of the mechanism responsible for shrinkage compensation.

In the process of hot casting, a decrease in the slip volume during solidification should be compensated by slip inflow under pressure. According to P. O. Gribovskii [1], this is accomplished by migration of the binder in the melted state into the solidification zone. However, at temperatures below 50°C, where most of the volume changes occur, the slip is in a solid-plastic state. Since migration of the liquid phase does not occur in such a layer because of the corresponding structure and rheological properties [3], it becomes obvious that the migration mechanism for compensation of the shrinkage will work only in the layer of liquid slip and on the interface between the solid and liquid phases. This raises the following question: What mechanism is responsible for the compensation of shrinkage in the technologically important (up to 85% of the total shrinkage) zone of the solid-plastic state of the casting?

A comparative analysis of the characteristics of castings (slip based on beryllium oxide and paraffin wax binder), obtained in different formation regimes (see Table 1), shows that this mechanism is plastic deformation of the solidifying layer of slip in the shaping volume of the casting mold under a pressure gradient which arises because the pressure in the region of the liquid slip is higher than the pressure in the solidification zone. The quite large increase of the apparent and relative density of the castings formed under pressure (regime 2) as compared with the castings obtained with solidification without the application of pressure (regime 1) shows that this mechanism makes a large contribution to the compensation of the volume changes.

On this basis the shrinkage compensation process during hot casting looks as follows to a first approximation. Initially, during the cast molding period when the slip flows from the working tank into the molding cavity with a temperature which is higher than the temperature of the mold, a cooled near-wall layer of high-viscosity slip, which does not participate in the flow, appears on the walls of the interior cavity of the mold as a result of heat-transfer from the hot slip to the cold mold. This layer, encompassing the walls of the mold, is washed by the flow of hot slip filling the casting mold and is relatively thin. For this reason, the thickness of the solidification front in this layer is minimal, which at this stage of the molding process permits compensation of the volume changes by a migration mechanism. The volume changes are compensated quite effectively, which is indicated by the absence of subsidence defects in the surface layers of the castings.

After filling has been completed, the dimensions of the zone of the thermoplastic state of the casting increase as the slip cools. When a pressure gradient with a definite magnitude is present in the molding cavity, a deformation mechanism compensating the shrinkage starts to operate in the layer of the slip which is in the plastic state (temperature below 54°C) together with the migration mechanism operating at the liquid—plastic mass boundary. The latter mechanism

TABLE 1.

Binder weight content, %	Apparent slip density, g/cm <sup>3</sup> , at 74°C		Apparent casting density, g/cm <sup>3</sup> , in regime*		Relative casting density, %, in regime	
	experimental data	computed values for a two-phase system	1	2	1	2
11.2	2.28	2.44	2.30	2.39	94.3	98.0
9.5	2.36	2.48	2.34	2.37	94.4	95.6

\* Regime (1) after being filled the molding cavity was disconnected from the filling tank and the casting solidified without the application of external pressure. Regime (2) after filling the slip was held under pressure (0.6 MPa) produced externally.

presupposes plastic deformation of this layer of slip, which, however, requires the application of a corresponding external force to produce a pressure gradient which is no less in magnitude than the plastic strength of the slip subjected to plastic deformation.

In summary, a migration—deformation mechanism of shrinkage compensation, and not a purely migration mechanism, operates in most cases in the process of slip solidification in hot casting of thermoplastic slips. The completeness of the compensation of the volume changes in the slip, which is very important for the flow of the casting process, the quality of the casting, the choice of the construction of the mold, and so forth, will be determined by the pressure gradient produced in the casting as it solidifies. This must be taken into account when designing casting setups and choosing the technological parameters for molding thermoplastic slips by the hot casting method.

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